1696 *Organometallics* 1987, *6*, 1696–1702

Low-Temperature X-ray Diffraction Studies of Bis(η^6-2,6-dimethylpyridine)titanium, -vanadium, and -chromium(I)

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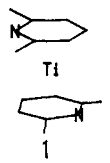
Received October 17, 1986

The molecular structures of three binary heterocyclic sandwich complexes have been determined by single-crystal X-ray diffraction at low temperature. Bis(η^6-2,6-dimethylpyridine)titanium, $(C_7H_9N)_2Ti$, crystallizes in the orthorhombic space group *Fdd*2 (*mm*2) with *a* = 14.110 (1) Å, *b* = 22.430 (2) Å, *c* = 8.203 (1) Å, and *Z* = 8. Bis(η^6-2,6-dimethylpyridine)vanadium, $(C_7H_9N)_2V$, crystallizes in the orthorhombic space group *Pbcn* (*mmm*) with *a* = 9.384 (2) Å, *b* = 10.441 (1) Å, *c* = 12.996 (3) Å, and *Z* = 4. Bis(η^6-2,6-dimethylpyridine)chromium tetrafluoroborate, $[(C_7H_9N)_2Cr][BF_4]$, crystallizes in the space group $P\bar{1}$ ($\bar{1}$) with *a* = 7.506 (1) Å, *b* = 9.346 (1) Å, *c* = 10.846 (1) Å, α = 78.242 (6)°, β = 87.575 (7)°, γ = 89.876 (6)°, and *Z* = 2. The metal–ring(center) distances are 1.774, 1.693, and 1.621 Å, respectively, while the metal–nitrogen distances are 2.119 ± 0.014 Å. A comparison is made between the metal–ring bonding in these complexes and the metal–ring bonding in bis(benzene)metal compounds.

Introduction

The synthesis of a series of $(2,6\text{-}Me_2C_5H_3N)M$ sandwich complexes where M is Ti (**1**),[2] V (**2**),[2] Cr(I) (**3**),[2] or Cr (**4A**, **4B**)[3] has been described. These compounds allow us to study the spectroscopic[2] and structural changes that occur when the valence electron count and/or the metal atom is varied while the ligands are kept constant. The structures of two isomers of bis(2,6-dimethylpyridine)chromium (**4A**, **4B**) have been reported by Riley and Davis.[4] We report here the results of low-temperature single-crystal X-ray diffraction studies of **1**, **2**, and **3** and discuss the results in terms of the π-donor and π-acceptor properties of η^6-pyridine.



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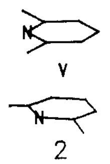

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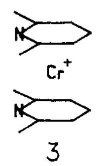

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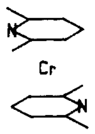
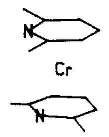


4 A



4 B

Experimental Section

General Data. All compounds were prepared as described in the preceding paper.[2] Precession photographs and automatic diffractometer peak search and indexing procedures were used in space group determination.[10] The crystals used for data collection were centered in the X-ray beam of an Enraf-Nonius CAD-4 diffractometer[5] and cooled in a nitrogen flow. The low-temperature apparatus was calibrated against a thermocouple placed in the sample position.

Raw intensity data were converted to structure factor amplitudes and their estimated standard deviations by correction for scan speed, background, and Lorentz and polarization effects.[11] The analytical forms of the scattering factor tables for the neutral atoms were used[6] in the refinement, and all non-hydrogen scattering factors were corrected for both the real and imaginary components of anomalous dispersion.[7] The quantity minimized by the least-squares program was $\sum[w(|F_o| - |F_c|)^2]$, where *w* is the weight of a given observation. The *p* factor,[8] used to reduce the weight of intense reflections, was set to 0.02 (**1** and **3**) or 0.03 (**2**) in the final stages of the refinement. A secondary extinction

Table I. Crystal and Data Collection Parameters[a]

	1 (Ti)	2 (V)	3 (Cr⁺)
a, Å	14.110 (1)	9.384 (2)	7.506 (1)
b, Å	22.430 (2)	10.441 (1)	9.346 (1)
c, Å	8.203 (1)	12.996 (3)	10.846 (1)
α, deg	90	90	78.242 (6)
β, deg	90	90	87.575 (7)
γ, deg	90	90	89.876 (6)
V, Å³	2596.0 (5)	1273.3 (7)	744.2 (2)
T, °C	−50 ± 4	−50 ± 4	−91 ± 4
space group	*Fdd*2	*Pbcn*	$P\bar{1}$
μ(calcd), cm⁻¹	6.3	7.33	7.87
fw	262.2	265.2	353.11
Z	8	4	2
d(calcd), g/cm³	1.34	1.38	1.58
size of cryst, mm	0.22 × 0.25 × 0.29	0.25 × 0.37 × 0.40	0.12 × 0.24 × 0.44
reflectns measd	+*h*,+*k*,±*l*	+*h*,+*k*,+*l*	±*h*,+*k*,±*l*
no. of unique reflectns	1492	1463	3411
no. of data ($F_o^2 > 3\sigma(F_o^2)$)	1404	1194	3073
parameters refined	114	115	283
R[b]	1.99%	2.60%	3.68%
wR[b]	2.59%	3.92%	5.43%
R (all data)	2.45%	3.73%	4.22%
secondary extinctn × 10⁷	29 (2)	5.6 (7)	9 (2)
GOF[b]	1.58	1.97	3.45

[a] Unit-cell parameters and their estimated standard deviations were derived by a least-squares fit to the setting angles of the unresolved Mo Kα components of 24 reflections with 2θ near 28°. In this and all subsequent tables the estimated standard deviations of all parameters are given in parentheses, right-justified to the least significant digit(s) given. Data were collected by using Mo Kα (λ = 0.71073 Å) radiation from a highly oriented graphite monochromater (2θ = 12.2°). θ–2θ scans were used to measure data from 3° to 55° (2θ) using variable scan width and variable horizontal aperture. Intensity standards were measured every hour of X-ray exposure time. Over the data collection period no decrease in intensity was observed for 1 and 2 and a 17% decay was observed for 3. Three orientation reflections were checked every 200 (1, 2) or 250 (3) measurements. Crystal orientation was redetermined if any of the reflections were offset from their predicted positions by more than 0.1°. Reorientation was performed once for 1 but was not needed for 2 or 3. [b] Reference 8.

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† Deceased.

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Table II. Fractional Coordinates and Isotropic Thermal Parameters (Å^2) for Bis(η^6-2,6-dimethylpyridine)metal Complexes[a]

atom	*x*	*y*	*z*	*B*	atom	*x*	*y*	*z*	*B*
$(C_7H_9N)_2Ti$ (**1**)									
Ti	0.25	0.25	0.0	1.72 (1)*	H3	0.410 (1)	0.207 (1)	−0.198 (3)	4.6 (5)
N	0.32124 (8)	0.32960 (5)	−0.0636 (2)	2.01 (2)*	H4	0.420 (1)	0.1872 (9)	0.095 (2)	3.5 (4)
C1	0.3502 (1)	0.30367 (8)	−0.3489 (2)	3.42 (3)*	H5	0.384 (1)	0.2655 (7)	0.273 (2)	2.1 (3)
C2	0.3564 (1)	0.28733 (6)	−0.1730 (2)	2.25 (2)*	H11	0.397 (1)	0.3328 (9)	−0.370 (3)	4.3 (4)
C3	0.3941 (1)	0.23384 (6)	−0.1158 (2)	2.49 (3)*	H12	0.291 (2)	0.321 (1)	−0.368 (3)	5.5 (5)
C4	0.3989 (1)	0.22203 (6)	0.0537 (2)	2.57 (3)*	H13	0.361 (2)	0.267 (1)	−0.412 (3)	6.2 (6)
C5	0.3783 (1)	0.26967 (7)	0.1625 (2)	2.31 (2)*	H71	0.372 (1)	0.4058 (9)	0.202 (3)	3.6 (4)
C6	0.34026 (9)	0.32273 (6)	0.1029 (2)	2.04 (2)*	H72	0.315 (2)	0.366 (1)	0.335 (3)	7.7 (8)
C7	0.3207 (1)	0.37588 (6)	0.2076 (2)	3.06 (3)*	H73	0.267 (1)	0.394 (1)	0.176 (3)	4.2 (5)
$(C_7H_9N)_2V$ (**2**)									
V	0.0	0.22109 (3)	0.25	1.85 (1)*	H3	−0.191 (2)	0.209 (1)	0.425 (1)	2.8 (4)
N	0.1011 (1)	0.3494 (1)	0.35480 (8)	2.25 (2)*	H4	−0.051 (3)	0.020 (2)	0.395 (2)	5.5 (5)
C1	−0.1238 (2)	0.4536 (2)	0.4004 (1)	4.17 (4)*	H5	0.197 (2)	0.049 (1)	0.354 (1)	3.6 (4)
C2	−0.0382 (2)	0.3334 (2)	0.3879 (1)	2.63 (3)*	H11	−0.115 (3)	0.518 (3)	0.349 (2)	9.9 (8)
C3	−0.0968 (2)	0.2114 (2)	0.4036 (1)	3.11 (3)*	H12	−0.212 (3)	0.442 (2)	0.398 (2)	8.9 (8)
C4	−0.0118 (2)	0.1012 (2)	0.3876 (1)	3.14 (3)*	H13	−0.129 (2)	0.483 (2)	0.468 (2)	6.9 (6)
C5	0.1341 (2)	0.1178 (2)	0.3642 (1)	2.71 (3)*	H71	0.353 (2)	0.326 (2)	0.267 (1)	4.1 (4)
C6	0.1875 (2)	0.2414 (1)	0.3474 (1)	2.22 (2)*	H72	0.390 (3)	0.185 (2)	0.294 (2)	6.4 (5)
C7	0.3402 (2)	0.2636 (2)	0.3205 (1)	3.01 (3)*	H73	0.397 (2)	0.292 (2)	0.384 (1)	3.9 (4)
$[(C_7H_9N)_2Cr][BF_4]$ (**3**)									
Cr	0.19419 (3)	0.30652 (3)	0.24919 (2)	1.56 (1)*	H71A	0.285 (5)	0.680 (4)	−0.035 (3)	7.3 (9)
N1A	0.2439 (2)	0.3645 (2)	0.0529 (1)	2.14 (3)*	H72A	0.104 (4)	0.620 (3)	0.030 (2)	4.2 (6)
C1A	0.2463 (4)	0.1133 (3)	0.0232 (2)	3.96 (5)*	H73A	0.228 (4)	0.686 (3)	0.114 (3)	4.9 (7)
C2A	0.3067 (3)	0.2255 (2)	0.0932 (2)	2.45 (4)*	H3B	0.148 (4)	0.052 (3)	0.417 (2)	3.9 (6)
C3A	0.4222 (3)	0.1927 (3)	0.1953 (2)	2.67 (4)*	H4B	0.255 (3)	0.234 (2)	0.513 (2)	2.2 (4)
C4A	0.4804 (3)	0.3065 (3)	0.2518 (2)	2.67 (4)*	H5B	0.151 (3)	0.477 (3)	0.427 (2)	3.3 (5)
C5A	0.4207 (3)	0.4499 (2)	0.2060 (2)	2.41 (4)*	H11B	−0.223 (4)	0.002 (3)	0.305 (2)	4.3 (6)
C6A	0.3033 (3)	0.4771 (2)	0.1053 (2)	2.11 (3)*	H12B	−0.129 (3)	0.078 (3)	0.167 (2)	2.6 (5)
C7A	0.2353 (3)	0.6262 (3)	0.0514 (2)	2.98 (4)*	H13B	−0.035 (4)	−0.023 (3)	0.255 (2)	4.0 (6)
N1B	−0.0873 (2)	0.3011 (2)	0.2664 (2)	1.89 (3)*	H71B	−0.227 (4)	0.562 (3)	0.323 (2)	4.1 (6)
C1B	−0.1081 (3)	0.0437 (2)	0.2561 (2)	3.10 (5)*	H72B	−0.036 (3)	0.634 (3)	0.282 (2)	3.2 (5)
C2B	−0.0269 (3)	0.1617 (2)	0.3099 (2)	2.20 (4)*	H73B	−0.152 (3)	0.566 (3)	0.190 (2)	2.9 (5)
C3B	0.1042 (3)	0.1352 (2)	0.4016 (2)	2.37 (4)*	B	−0.3797 (2)	0.2198 (2)	0.6200 (2)	2.69 (4)*
C4B	0.1699 (3)	0.2500 (3)	0.4515 (2)	2.42 (4)*	F1	−0.4251 (4)	0.3597 (2)	0.5627 (3)	5.70 (6)*
C5B	0.1024 (3)	0.3922 (2)	0.4090 (2)	2.18 (4)*	F1A	−0.3497 (7)	0.3490 (4)	0.5358 (4)	4.98 (6)
C6B	−0.0302 (2)	0.4140 (2)	0.3178 (2)	1.90 (3)*	F2	−0.2306 (3)	0.1957 (3)	0.6905 (2)	5.54 (6)*
C7B	−0.1148 (3)	0.5593 (2)	0.2737 (2)	2.44 (4)*	F2A	−0.2021 (4)	0.2202 (6)	0.6425 (5)	5.0
H3A	0.456 (4)	0.089 (3)	0.233 (2)	4.2 (6)	F3A	−0.5261 (5)	0.2349 (6)	0.6958 (4)	5.26 (7)
H4A	0.548 (3)	0.289 (3)	0.323 (2)	2.9 (5)	F3B	−0.5267 (5)	0.1625 (5)	0.6902 (4)	5.3
H5A	0.456 (3)	0.529 (3)	0.249 (2)	2.8 (5)	F3C	−0.4752 (6)	0.1853 (6)	0.7341 (3)	5.3
H11A	0.323 (4)	0.127 (4)	−0.062 (3)	6.1 (8)	F4	−0.4165 (3)	0.1144 (2)	0.5536 (2)	5.56 (5)*
H12A	0.248 (4)	0.021 (3)	0.073 (3)	5.2 (7)	F4A	−0.3454 (7)	0.1472 (4)	0.5230 (3)	5.0
H13A	0.112 (4)	0.132 (3)	−0.007 (3)	4.8 (7)					

[a] Numbers of hydrogen atoms correspond to the carbon atoms to which they are bound, e.g., C7A–H71A. Temperature factors with an asterisk indicate an isotropic equivalent $\{^4/_3[a^2B(1,1) + b^2B(2,2) + c^2B(3,3) + ab \cos \gamma\, B(1,2) + ac \cos \beta\, B(1,3) + Bc \cos \alpha\, B(2,3)]\}$ for an atom refined with anisotropic thermal parameters (see supplementary material).

parameter[9] was refined in the final cycles of least squares. Cell parameters and specific data collection parameters are given in Table I. Positional and isotropic thermal parameters of the atoms are presented in Table II. Hydrogen atom positions are uncorrected. Lists of F_o/F_c and anisotropic thermal parameters are available in the supplementary material.

Crystal Structure of 1. Crystals suitable for X-ray work were obtained by sublimation under vacuum. Fragments cleaved from some of these crystals were mounted in capillaries in an inert-atmosphere glovebox, and the capillaries were flame sealed.

The structure was solved by Patterson methods using a data set with Friedel pairs averaged (799 data) and refined via standard least-squares and Fourier techniques. Inspection of azimuthal scan data showed a variation of ±1% for the average curve. No correction for absorption was applied. In a difference Fourier map calculated following refinement of all non-hydrogen atoms with anisotropic thermal parameters, peaks corresponding to the expected positions of all of the hydrogen atoms were found and

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(2) (a) Wucherer, E. J.; Muetterties, E. L. *Organometallics*, preceeding paper in this issue. (b) Wucherer, E. J. Ph.D. Thesis, UC—Berkeley, 1985.

(3) Simons, L. H.; Riley, P. E.; Davis, R. E.; Lagowski, J. J. *J. Am. Chem. Soc.* **1976**, *98*, 1044.

(4) Riley, P. E.; Davis, R. E. *Inorg. Chem.* **1976**, *15*, 2735.

(5) University of California Chemistry Department X-ray Crystallographic Facility (CHEXRAY) Enraf-Nonius CAD-4 diffractometer and software as described in the *CAD-4 Operations Manual*, Enraf-Nonius, Delft, Nov 1977, updated Jan 1980.

(6) Cromer, D. T.; Waber, J. T. *International Tables for X-ray Crystallography*; Kynoch: Birmingham, 1974; Vol. IV, Table 2.2B.

(7) Cromer, D. T., ref 6, Table 2.3.1

(8) $R = \sum||F_o| - |F_c||/\sum|F_o|$, $wR = [\sum w(|F_o| - |F_c|)^2/\sum wF_o^2]^{1/2}$, and GOF = $[\sum w(|F_o| - |F_c|)^2/(n_o - n_v)]^{1/2}$, where n_o is the number of observations, n_v is the number of variable parameters, and the weights w are given by $w = 4F_o^2/\sigma^2(F_o^2)$, where $\sigma^2(F_o^2) = [\sigma_o^2(F_o^2) + (pF_o^2)^2]$ (p is the factor used to lower the weight of intense reflections).

(9) Zachariesen, W. H. *Acta Crystallogr.* **1963**, *16*, 1139.

(10) Roof, R. B. *A Theoretical Extension of the Reduced-Cell Concept in Crystallography*; Publication LA-4038, Los Alamos Scientific Laboratory, Los Alamos, 1969.

(11) The data reduction formulas are $F_o^2 = \omega(C - 2B)/Lp$, $\sigma(F_o^2) = \omega(C + 4B)^{1/2}/Lp$, $F_o = (F_o^2)^{1/2}$, and $\sigma_o(F) = \sigma_o(F_o^2)/2F_o$, where C is the total count in the scan, B the sum of the two background counts, ω the scan speed used in deg/min, and $1/Lp = (\sin 2\theta)(1 + \cos^2 2\theta_m)/(1 + \cos^2 2\theta_m - \sin^2 2\theta)$ is the correction for Lorentz and polarization effects for reflections with the scattering angle 2θ and radiation monochromatized with a 50% perfect single-crystal monochromater with the scattering angle $2\theta_m$.

were included in the least-squares refinement. Refinement continued against the unaveraged unique data, and the model was tested for the correct polarity for this crystal.

Inspection of the residuals ordered in ranges of $(\sin\theta)/\lambda$, $|F_o|$, and parity and value of the individual indexes showed no unusual features or trends. The largest peak in the difference Fourier map had an electron density of 0.22 e/Å^3.

Crystal Structure of 2. Blocky, air-sensitive crystals of the compound were obtained by sublimation under vacuum. Fragments cleaved from some of these crystals were mounted in capillaries in an inert-atmosphere glovebox, and the capillaries were flame-sealed.

The structure was solved by substitution of the coordinates of the isomorphous chromium compound **4B**[4] and refined via standard least-squares and Fourier techniques. In a difference Fourier map calculated following refinement of all non-hydrogen atoms with anisotropic thermal parameters, peaks corresponding to the expected positions of all of the hydrogen atoms were found and were included in the least-squares refinement. Inspection of azimuthal scan data showed a variation of ±2.5% for the average curve. No correction for absorption was applied.

Inspection of the residuals ordered in ranges of $(\sin\theta)/\lambda$, $|F_o|$, and parity and value of the individual indexes showed those reflections with $(h + k)$ odd were much weaker and gave poorer agreement, but no other unusual features or trends were noted. The largest peak in the difference Fourier map had an electron density of 0.26 e/Å^3. It was located between C2 and C3.

Crystal Structure of 3. Pale orange needlelike and platelike crystals of the compound were obtained by slow crystallization from toluene/methylene chloride (2:3 v/v) solution. Fragments cleaved from some of these crystals were mounted on glass fibers by using polycyanoacrylate cement.

Inspection of the intensity standards showed a monotonic, nearly isotropic decrease to 0.83 of the original intensity. The data were corrected for this decay. Inspection of the azimuthal scan data showed a variation, $I_{\min}/I_{\max} = 0.88$, for the average curve. An absorption correction based on the measured shape and size of the crystal and an 10 × 12 × 6 Gaussian grid of internal points was applied to the data ($T_{\max} = 0.919$, $T_{\min} = 0.691$).

The structure was solved by Patterson methods and refined via standard least-squares and Fourier techniques. The assumption that the space group was centric was confirmed by the successful solution and refinement of the structure. In a difference Fourier map calculated following refinement of all non-hydrogen atoms with anisotropic thermal parameters, peaks corresponding to the expected positions of all of the hydrogen atoms were found. Hydrogen atoms were refined in least squares with isotropic thermal parameters. Inspection of the electron density around the anion revealed the necessity for a disordered model for the BF_4^-. B to F distances were constrained to be equal, and F to F distances were constrained to prevent instability in the model. Three fluorine positions had occupancies of $^2/_3$ and were allowed to refine with anisotropic thermal parameters. All other fluorine positions were of $^1/_3$ occupancy and were refined with isotropic thermal parameters constrained to be equal within each of the two sets of F1A, F2A, F4A and F3A,B,C.

Inspection of the residuals ordered in ranges of $(\sin\theta)/\lambda$, $|F_o|$, and parity and value of the individual indexes showed no unusual features or trends. The largest peaks in the difference Fourier map had an electron density ±0.6 e/Å^3. All were located near the BF_4 anion, indicating that the disorder model was not completely satisfactory. There was, however, no obvious way to improve it, so refinement was concluded.

Results

Inspection of the data collection parameters and the atomic coordinates (Table I and II) shows that the structures are quite precise and that bond distances are reliable to 0.002 Å (Table III). The internal consistency of chemically equivalent bond parameters, for example, the distribution of N–C bond distances about the mean, indicates that the determinations are also accurate models of the solid-state structures of **1**, **2**, and **3**.

Table III. Bond Distances (Å) for 1, 2, and 3

		distances			
				3 (Cr)	
atom	atom	1 (Ti)	2 (V)	ring A	ring B
M	N	2.114 (1)	2.133 (1)	2.105 (1)	2.113 (1)
M	C2	2.229 (1)	2.171 (1)	2.132 (1)	2.139 (1)
M	C3	2.273 (1)	2.195 (1)	2.137 (1)	2.141 (1)
M	C4	2.236 (1)	2.186 (1)	2.149 (1)	2.150 (1)
M	C5	2.291 (1)	2.224 (1)	2.143 (1)	2.140 (1)
M	C6	2.235 (1)	2.178 (1)	2.128 (1)	2.143 (1)
M	CNTR	1.774	1.693	1.616	1.626
N	C2	1.397 (2)	1.386 (1)	1.373 (2)	1.375 (1)
N	C6	1.400 (2)	1.392 (1)	1.377 (1)	1.367 (1)
C1	C2	1.491 (2)	1.498 (2)	1.496 (2)	1.491 (2)
C2	C3	1.394 (2)	1.403 (2)	1.419 (2)	1.415 (2)
C3	C4	1.417 (2)	1.415 (2)	1.411 (2)	1.396 (2)
C4	C5	1.422 (2)	1.413 (2)	1.409 (2)	1.415 (2)
C5	C6	1.394 (2)	1.401 (2)	1.415 (2)	1.418 (1)
C6	C7	1.495 (2)	1.494 (2)	1.495 (2)	1.495 (2)
C3	H3	0.94 (2)	0.93 (1)	1.01 (2)	0.83 (2)
C4	H4	0.90 (2)	0.93 (2)	0.93 (2)	0.93 (1)
C5	H5	0.92 (2)	0.93 (1)	0.99 (2)	0.93 (2)
C1	H11	0.94 (2)	0.95 (2)	1.05 (2)	1.03 (2)
C1	H12	0.94 (3)	0.84 (2)	0.92 (2)	0.98 (2)
C1	H13	0.98 (3)	0.94 (2)	1.07 (2)	0.83 (2)
C7	H71	0.98 (2)	0.96 (2)	1.02 (3)	0.98 (2)
C7	H72	1.07 (3)	1.00 (2)	1.03 (2)	0.94 (2)
C7	H73	0.89 (2)	1.03 (2)	0.97 (2)	0.95 (2)

BF_4^- (3)

atom	atom	distance	atom	atom	distance
B	F1	1.377 (1)	B	F3B	1.360 (2)
B	F1A	1.370 (2)	B	F3C	1.383 (2)
B	F2	1.374 (1)	B	F4	1.369 (1)
B	F2A	1.365 (2)	B	F4A	1.379 (2)
B	F3A	1.368 (2)			

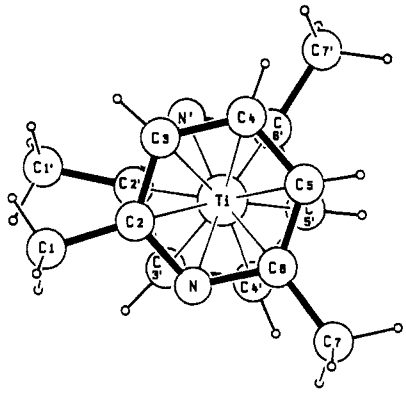

Figure 1. Conformation of $(C_7H_9N)_2Ti$ (1). The twofold axis is approximately horizontal in this view.

The 16-electron titanium compound **1** has C_2 site symmetry and lies on a crystallographic twofold axis in the space group *Fdd*2. The twofold axis is approximately parallel to the molecular C1, C2, and C5 direction and passes through the titanium atom. This produces a nitrogen–center–center′–nitrogen′ torsional angle of 140.1°. The staggered configuration (Figure 1) is unusual for sandwich complexes.[12]

The distances between the titanium atom and the ring atoms (Table III) are best discussed by using atoms C2, C3, C5, and C6 to define a plane. This plane is 1.772 (0) Å above the titanium atom and is not rigorously parallel to its twofold image (Table V), rather it is tilted by about 6° so that N and C3′ have the shortest ring–ring′ distance. The nitrogen atom and para carbon atom (C4) are bent by more than 0.1 Å out of the C(2,3,5,6) plane toward the titanium atom. The titanium atom is displaced 0.07 Å

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[12] Muetterties, E. L.; Bleeke, J. R.; Wucherer, E. J.; Albright, T. A. *Chem. Rev.* **1982**, *82*, 499.

Table IV. Bond Angles (deg) for 1, 2, and 3

			angle			
					3 (Cr)	
atom 1	atom 2	atom 3	1 (Ti)	2 (V)	ring A	ring B
CNTR	M	CNTR′	176.9	176.5	174.6	
C2	N	C6	118.9 (1)	118.23 (9)	120.0 (1)	120.20 (9)
N	C2	C1	115.7 (1)	116.0 (1)	116.0 (1)	116.4 (1)
N	C2	C3	120.2 (1)	121.6 (1)	121.1 (1)	120.4 (1)
C1	C2	C3	124.0 (1)	122.3 (1)	122.8 (1)	123.1 (1)
C2	C3	C4	120.6 (1)	119.7 (1)	119.2 (1)	120.2 (1)
C3	C4	C5	117.8 (1)	118.6 (1)	119.0 (1)	118.8 (1)
C4	C5	C6	120.0 (1)	119.6 (1)	119.8 (1)	119.3 (1)
N	C6	C5	120.7 (1)	121.8 (1)	120.7 (1)	120.9 (1)
N	C6	C7	115.9 (1)	116.69 (9)	116.5 (1)	116.78 (9)
C5	C6	C7	123.4 (1)	121.5 (1)	122.8 (1)	122.3 (1)
C2	C3	H3	114 (1)	116.5 (8)	121.7 (9)	117 (1)
C4	C3	H3	125 (1)	123.8 (8)	118.9 (9)	122 (1)
C3	C4	H4	123 (1)	120 (1)	121.9 (9)	121.0 (8)
C5	C4	H4	119 (1)	121 (1)	118.9 (9)	120.2 (8)
C4	C5	H5	121.9 (9)	123.1 (8)	119.2 (8)	124.6 (9)
C6	C5	H5	117.8 (9)	117.2 (8)	120.9 (8)	115.4 (9)
C2	C1	H11	108 (1)	118 (2)	108 (1)	112.4 (9)
C2	C1	H12	109 (1)	114 (1)	111 (1)	110.7 (8)
C2	C1	H13	107 (1)	114 (2)	112 (1)	110 (1)
H11	C1	H12	107 (2)	99 (2)	116 (2)	111 (1)
H11	C1	H13	112 (2)	116 (2)	104 (1)	110 (1)
H12	C1	H13	113 (2)	92 (2)	107 (2)	103 (1)
C6	C7	H71	112 (1)	113 (1)	119 (1)	108 (1)
C6	C7	H72	114 (1)	113 (1)	110.0 (9)	109.8 (9)
C6	C7	H73	111 (1)	110.8 (9)	111 (1)	109.2 (9)
H71	C7	H72	104 (2)	104 (2)	98 (1)	112 (1)
H71	C7	H73	107 (2)	109 (1)	114 (2)	104 (1)
H72	C7	H73	108 (2)	106 (1)	101 (1)	114 (1)

BF_4 (3)

atom 1	atom 2	atom 3	angle	atom 1	atom 2	atom 3	angle
F1	B	F2	120.3 (2)	F2	B	F3B	110.4 (2)
F1	B	F2A	107.7 (2)	F2	B	F3C	85.6 (2)
F1	B	F3A	82.0 (3)	F2	B	F4	115.3 (1)
F1	B	F3B	105.9 (2)	F2	B	F4A	104.2 (2)
F1	B	F3C	107.6 (2)	F2A	B	F3A	130.8 (2)
F1	B	F4	115.0 (1)	F2A	B	F3B	133.7 (2)
F1	B	F4A	105.4 (2)	F2A	B	F3C	108.8 (2)
F1A	B	F2	106.0 (2)	F2A	B	F4	110.1 (2)
F1A	B	F2A	87.1 (2)	F2A	B	F4A	90.3 (2)
F1A	B	F3A	108.8 (2)	F3A	B	F4	108.3 (2)
F1A	B	F3B	132.4 (2)	F3A	B	F4A	134.7 (2)
F1A	B	F3C	132.4 (2)	F3B	B	F4	82.7 (2)
F1A	B	F4	108.2 (2)	F3B	B	F4A	110.4 (2)
F1A	B	F4A	88.5 (2)	F3C	B	F4	107.5 (2)
F2	B	F3A	110.1 (2)	F3C	B	F4A	134.0 (2)

from the center of the C(2,3,5,6) rectangle toward the nitrogen atom. Hydrogen atom H4 follows the C4 movement and bends toward the metal, while hydrogen atoms H3 and H5 remain in the plane. The methyl substituents bend out of the plane away from the titanium atom.

The N–C2 and N–C6 distances are as long as or slightly longer than the C2–C3 and C5–C6 distances while the longest distances are between C3, C4, and C5 (Table III). The intra-ring bond distances are expected to expand isotropically upon coordination to the metal.[12] The expansion in this case is quite anisotropic as the nitrogen–carbon ring distances are normally *ca.* 0.05 Å shorter than carbon–carbon distances.[13–15] The ring–methyl and carbon–hydrogen distances are as expected.

There are several close intra- and intermolecular contacts in the structure of 1 (Table VI). The nitrogen atom

Table V. Least-Squares Planes for Bis(η^6-2,6-dimethylpyridine)metal[a]

	Δ			
			3 (Cr)	
atom	1 (Ti)[b]	2 (V)[c]	ring A[d]	ring B[e]
C2	0.002 (1)*	−0.006 (1)*	0.006 (2)*	0.003 (2)*
C3	−0.002 (1)*	0.006 (2)*	−0.006 (2)*	−0.003 (2)*
C5	0.002 (1)*	−0.006 (1)*	0.006 (2)*	0.004 (2)*
C6	−0.002 (1)*	0.006 (1)*	−0.006 (2)*	−0.004 (2)*
M	−1.772 (0)	1.692 (0)	−1.616 (0)	1.626 (0)
N	−0.124 (1)	0.063 (1)	−0.044 (2)	0.050 (2)
C1	0.133 (2)	−0.023 (2)	0.074 (3)	−0.050 (2)
C4	−0.109 (1)	0.061 (2)	0.001 (2)	0.000 (2)
C7	0.172 (2)	−0.037 (2)	0.006 (2)	−0.075 (2)
H3	0.00 (2)	−0.04 (2)	−0.09 (3)	0.09 (3)
H4	−0.16 (2)	0.10 (2)	−0.08 (2)	−0.02 (2)
H5	0.00 (2)	0.00 (2)	−0.04 (2)	0.14 (3)

[a] Atoms denoted with an asterisk were used to define the plane. All distances in Å. Equations of planes refer to orthogonalized coordinates. [b] Plane defined by $0.9188x + 0.3919y - 0.0467z = 7.2108$. [c] Plane defined by $-0.2575x - 0.0530y - 0.9648z = -4.9291$. [d] Plane defined by $0.7601x + 0.0353y - 0.6488z = 1.2206$. [e] Plane defined by $0.6852x + 0.0257y - 0.7278z = -2.3747$.

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(13) Bak, B.; Hansen-Nygaard, L.; Rastrup-Andersen, J. *J. Mol. Spectrosc.* **1958**, *2*, 361.

(14) Mootz, D.; Wussow, H. -G. *J. Chem. Phys.* **1981**, *75*, 1517.

(15) Lenstra, A. T. H.; Petit, G. H. *Cryst. Struct. Commun.* **1979**, *9*, 725.

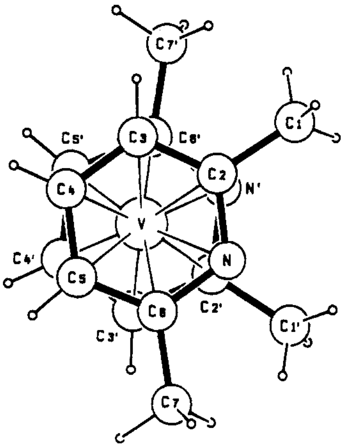

Figure 2. Conformation of $(C_7H_9N)_2V$ (2). The twofold axis is approximately horizontal in this view.

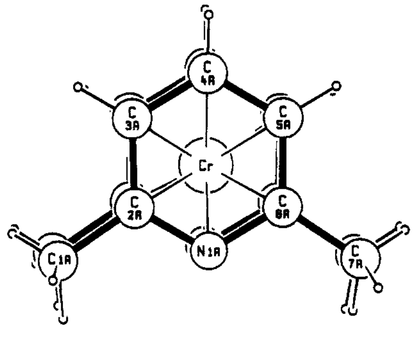

Figure 3. Conformation of $(C_7H_9N)_2Cr^+$ (3). The "B" ring lies directly beneath the "A" ring.

is surrounded by three hydrogen atoms at ca. 2.55 Å. Two of the hydrogen contacts are with hydrogens on methyl groups directly adjacent to the nitrogen atom. The third contact is a hydrogen bond[16] with H4′ on a neighboring ring.

Bis(η^6-2,6-dimethylpyridine)vanadium (2) is isostructural with the chromium complex **4B**.[4] Like the titanium compound 1, it possesses C_2 point symmetry and lies on a crystallographic twofold axis. The twofold axis passes through the vanadium atom and is approximately parallel with the mid(N–C2)–mid(C4–C5) vector (Figure 2). The two ligand rings are 13° from eclipsed with an N-Center–center′-N′ torsional angle of 47°.

The intra-ring distances in 2 are closer to the values predicted on the basis of the atomic covalent radii. Unlike 1, the nitrogen–carbon bond distances are shorter than all of the carbon–carbon distances, but the expansion upon coordination is still much larger for the C–N bonds than for the C–C bonds.

Vanadium–ring bond distances again indicate that the metal atom is not equally bonded to all ring atoms. The ring planes defined by C2, C3, C5, and C6 are tilted by 6°, with the nitrogen (N, N′) and ortho-carbon atoms (C2, C2′) having the shortest inter-ring contacts. The vanadium atom lies 1.692 (0) Å from the planes and is displaced only slightly off center toward the nitrogen atoms. The nitrogen and para-carbon atom (C4) are again drawn out of the ring plane toward the metal atom, although not as far as for 1 (Table V). The hydrogen and methyl substituents are displaced in the same directions as observed for 1, but the displacements are not as large.

Table VI. Intra- and Intermolecular Contact Distances (Å) for 1, 2, and 3

atom	atom	distance	sym
	$(C_7H_9N)_2Ti$ (1)[a]		
N	H73	2.56 (2)	i
N	H12	2.54 (2)	i
N	C3	3.382 (2)	ii
C2	C2	3.438 (2)	ii
N	H4	2.53 (2)	iii
N	C4	3.401 (2)	iii
C6	C7	3.650 (2)	iv
N	C7	3.663 (2)	iv
C4	C1	3.675 (2)	v
C3	C5	3.691 (2)	vi
	$(C_7H_9N)_2V$ (2)[b]		
N	C2	3.213 (1)	i
N	N	3.319 (2)	i
C3	C6	3.386 (2)	i
C4	C5	3.472 (2)	i
C7	C7	3.514 (2)	ii
C1	C1	3.610 (3)	iii
C4	C4	3.612 (2)	iv
C3	C7	3.644 (2)	v
	$[(C_7H_9N)_2Cr][BF_4]$ (3)[c]		
N1B	H73B	2.50 (2)	i
N1B	H12B	2.56 (2)	i
N1A	H72A	2.58 (2)	i
C4A	C4B	3.084 (1)	i
C5A	C5B	3.150 (1)	i
C3A	C3B	3.172 (2)	i
N1A	N1B	3.295 (1)	i
C6A	C6B	3.300 (1)	i
C2A	C2B	3.330 (2)	i
C7A	C7B	3.459 (2)	i
C1A	C1B	3.556 (2)	i
F4A	H3B	2.38 (2)	ii
F1A	H5B	2.32 (2)	iii
F3B	H3A	2.40 (2)	ii
F4A	H4A	2.46 (2)	iv
F3A	H5A	2.47 (2)	iii
F1	H5A	2.48 (2)	iii
N1B	C4A	3.256 (1)	iv
C3B	C3B	3.305 (2)	ii
C5B	C5B	3.418 (2)	iii
C5B	C7B	3.568 (2)	iii
N1B	C7A	3.598 (2)	v
C6A	C6A	3.628 (2)	vi
N1A	C7B	3.640 (2)	v

[a] (i) x, y, z; (ii) $^1/_2 - x, {}^1/_2 - y, z$; (iii) $^3/_4 - x, {}^1/_4 + y, -{}^1/_4 + z$; (iv) $^1/_4 + x, {}^3/_4 - y, -{}^1/_4 + z$; (v) $1 - x, {}^1/_2 - y, {}^1/_2 + z$; (vi) $1 - x, {}^1/_2 - y, -{}^1/_2 + z$. [b] (i) $-x, y, {}^1/_2 - z$; (ii) $1 - x, y, {}^1/_2 - z$; (iii) $-x, 1 - y, 1 - z$; (iv) $-x, -y, 1 - z$; (v) $-{}^1/_2 + x, {}^1/_2 - y, 1 - z$. [c] (i) x, y, z; (ii) $-x, -y, 1 - z$; (iii) $-x, 1 - y, 1 - z$; (iv) $1 - x, y, z$; (v) $-x, 1 - y, -z$; (vi) $1 - x, 1 - y, -z$.

Compound 2 also has short intermolecular contacts, but the nitrogen atom is not involved. The intermolecular interactions here are only between CH and CH_3 groups.

The second 17-electron complex bis(η^6-2,6-dimethylpyridine)chromium tetrafluoroborate (3) consists of discrete anionic and cationic units. The anion could only be refined by using a disordered model and does not appear to have any unusual characteristics. The cationic sandwich complex has nearly perfect C_{2v} site symmetry although none is crystallographically required. The N1A–center A–center B–N1B torsion angle is 0.7°. Ring carbon atoms C4A and C4B have the shortest intramolecular contact, a result of the ring planes being tipped 6.4°.

Around the ring the bond distances are longer than in an uncomplexed ring, as expected by analogy with the structures of bis(η^6-benzene)metal compounds. The metal–ring bonding in this compound is different than in 1 and 2. Carbons C4A and C4B are located in the ring planes. They are not bent toward the metal atom as in 1 and 2 and have the longest metal–carbon bond distances

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[16] Taylor, R.; Kennard, O. *Acc. Chem. Res.* **1984**, *17*, 320 and references therein.

Table VII. Bond Distances (Å) of Pyridine Rings

	compd	M–ring[a]	M–N	N–C	ortho C–meta C	meta C–para C	ref
1	C_5H_5N (gas phase)			1.3402 (2)	1.3945 (2)	1.3944 (2)	*b*
2	C_5H_5N (crystal)			1.336 (3)	1.381 (5)	1.378 (5)	*c*
3	2,6-$(CH_3)_2$-3,5-$(C_2H_3O)_2C_5N$			1.335	1.404	1.378	*d*
4	[2,6-$(CH_3)_2C_5H_3N]_2Cr^+$	1.616 (0)	2.105 (1)	1.375 (3)	1.417 (3)	1.410 (2)	*e*
		1.626 (0)	2.113 (1)	1.371 (6)	1.417 (2)	1.405 (13)	*e*
5	[2,6-$(CH_3)_2C_5H_3N]_2Cr$ (A)	1.622 (1)	2.151 (6)	1.39 (2)	1.379 (9)	1.41 (2)	*f*
6	[2,6-$(CH_3)_2C_5H_3N]_2Cr$ (B)	1.635 (1)	2.131 (3)	1.380 (3)	1.392 (3)	1.40 (1)	*f*
7	[2,6-$(CH_3)_2C_5H_3N]_2V$	1.692 (0)	2.133 (1)	1.389 (4)	1.402 (2)	1.414 (2)	*e*
8	[2,6-$(CH_3)_2C_5H_3N]_2Ti$	1.772 (0)	2.114 (1)	1.398 (2)	1.394 (2)	1.420 (3)	*e*
9	[2,6-$(t$-$C_4H_9)_2C_5H_3N]Cr(CO)_3$	1.714	2.212 (4)	1.365 (7)	1.413 (7)	1.382 (6)	*g*

[a] Plane defined by C2, C3, C5, and C6 for entries 4, 6, 7, and 8. [b] Reference 13. [c] Reference 14. [d] Reference 15. [e] This work. [f] Reference 4. [g] Reference 21.

in the molecule. Projecting the metal atom onto the C2A, C3A, C5A, C6A or C2B, C3B, C5B, C6B planes shows that the chromium atom lies on the center point and not toward the nitrogen atom as seen for 1 and 2. The nitrogen atoms N1A and N1B are again bent out of their respective ring planes toward the chromium atom. The hydrogen atoms on the ring carbon atoms are, with one exception, bent toward the metal, and the methyl groups are bent away. Since the ligand rings are eclipsed and the chromium–ring distances are only 1.616 (0) (ring A) and 1.626 (0) Å (ring B), each of the atoms in the ligand rings has a short contact distance to the corresponding atom in the other ring. This ring A–ring B interaction does not appear to influence the structure of the ring itself, but the methyl carbon atoms do bend out of the ring plane and the methyl hydrogen atoms are rotated (see 1) such that they are fairly close to the nitrogen atoms (Table VI).

Discussion

The three structural determinations reported here, bis(η^6-2,6-dimethylpyridine)titanium, -vanadium, and -chromium(1+) (1–3), and the two previously reported structures of bis(η^6-2,6-dimethylpyridine)chromium (4A,B)[4] have all been carried out at low temperature and, except for 4A, are of high precision. By examining the structural changes that occur for the different metal atoms and electron counts, we can study the bonding in these sandwich complexes.

As in the previous paper[2] the bis(η^6-2,6-dimethylpyridine)metal compounds will be compared to bis(η^6-benzene)metal complexes. The frontier π orbitals of benzene and pyridine are shown in Figure 4.[17] The electronegative nitrogen atom of pyridine stabilizes the frontier π and π^* orbitals of pyridine relative to benzene. Consequently, for a given reference metal, we can expect pyridine to be a poorer π donor and a better π acceptor than benzene.

In bis(benzene)metal complexes the occupied ligand E_{1g} orbitals and the unoccupied ligand E_{2u} orbitals build cylindrically symmetric sets of π-donor and π-acceptor orbitals that interact with the metal d_{xz}, d_{yz} and d_{xy}, $d_{x^2-y^2}$ orbitals, respectively.[18] In bis(pyridine)metal complexes the frontier orbitals can be constructed in the same way, but the frontier orbitals of pyridine do not form cylindrically symmetric (degenerate) sets so that the ring–metal bonding cannot be perfectly cylindrically symmetric.

The HOMO of bis(benzene)chromium, -chromium(I), and -vanadium is mainly composed of the metal d_{z^2} orbital.[18] This orbital points directly at the center of the ring and is almost completely metal–ring nonbonding. Spectroscopic evidence indicates that the same is true for 1, 2, 3, and 4.[2] This means that the occupation of this orbital by zero, one, or two electrons (forming formally 16-, 17-, and 18-electron complexes) has no direct effect on the metal–ring bonding in bis(benzene)- and bis(pyridine)-metal complexes.[18] The variations in the metal–ring and intra-ring bonding that occur for compounds 1–4 are therefore not a result of the formal valence electron count but rather are related to the variation of the energy of the metal d_{xz}, d_{yz}, d_{xy}, and $d_{x^2-y^2}$ orbitals. The energy of these metal d orbitals is controlled by the effective nuclear charge which the metal center exerts on the d orbitals. Entries 4–8 in Table VII are arranged in order of decreasing effective nuclear charge.

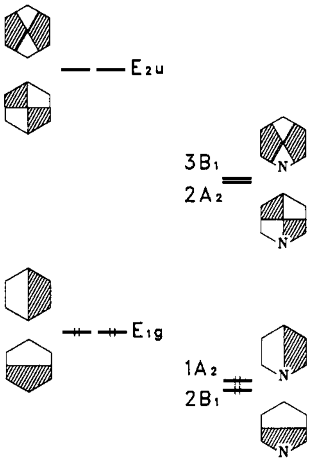

Figure 4. Frontier π-orbitals of benzene (left) and pyridine (right).

Chromium(I) exerts the strongest effective nuclear charge on the d orbitals so we expect electron donation from the pyridine $^2B_1$ and $^1A_2$ orbitals to the metal d_{xz} and d_{yz} orbitals to be an important bonding interaction in 3. Conversely, titanium has the lowest effective nuclear charge of the metals studied, so acceptance of electron density from the metal d orbitals into the π^*-ring orbitals is probably most important in 1.

Intra-ring Bonding. Coordination of the pyridine ring in 3 results in an isotropic expansion of the inter-ring distances of about 0.035 Å (compare entries 2 and 4, Table VII), similar to the expansion observed when benzene coordinates to chromium.[12] Since the expansion is isotropic, it does not appear that any one ring orbital has a preferential bonding interaction with the metal d orbitals. This is not the case for the titanium complex 1.

In 1 the nitrogen–ortho carbon and meta carbon–para carbon distances are expanded by 0.062 (5) and 0.042 (8) Å, respectively, while the ortho carbon–meta carbon distances only expand by 0.013 (7) Å. Since we expect a

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(17) Jorgensen, W. L.; Salem, L. *The Organic Chemists Book of Orbitals*; Academic: New York, 1973.

(18) a) Weber, J.; Geoffroy, M.; Goursot, A.; Penigault, E. *J. Am. Chem. Soc.* **1978**, *100*, 3995. b) Green, J. C. *Struct. Bonding (Berlin)* **1981**, *43*, 37.

strong metal to ring electron donor interaction for this complex, the observed long–short–long expansion could be the result of the metal d_{xz} or d_{yz} orbitals donating electron density into the ring 3B1 π^* orbital.

The compounds 4 and 2 seem to represent a compromise between the two extremes of 1 and 3.

Ring–Metal–Ring Configuration. Compound 3 exhibits an exact sym-eclipsed configuration (Figure 3) such that each ring atom lies directly over its corresponding atom in the opposing ring. Since 3 has the shortest metal–ring(plane) distances, the ring A–ring B contacts are short (Table VI) and the methyl substituents are packed tightly together. This configuration also results in the parallel alignment of the pyridine dipoles. Clearly there is some ring–metal bonding interaction which counterbalances these seemingly repulsive interactions.

Bis(η^6-2,6-dimethylpyridine)chromium (4) exhibits both an anti-eclipsed (**4A**) and a noneclipsed (**4B**) configuration.[4] The anti-eclipsed configuration (**4A**) appears to be stabilized by an intermolecular hydrogen bond,[19] while the structure of **4B** does not show any inter- or intramolecular interactions which might stabilize the noneclipsed orientation. Compounds 1 and 2 have noneclipsed rings with the orientation in 1 further stabilized by an intermolecular hydrogen bond.

Most bis(η^6-arene)metal complexes have an eclipsed configuration,[12] although the exact bonding interactions responsible have not been identified. A few compounds with electron-withdrawing (CF_3) substituents on the arene are not eclipsed. This has been attributed to steric repulsion between substituents on opposing rings.[20] Our results here indicate that the orbital interactions that favor eclipsing are the ring to metal electron-donating interactions. Benzene is a better electron donor than pyridine, and most bis(benzene)metal derivatives are eclipsed. Pyridine is a poorer electron donor, and so only 3 with the high effective nuclear charge on the chromium(1+) atom has sufficient ring to metal donation to favor the eclipsed orientation.

The noneclipsed orientation in **4B**, 2, and 1 could be due to a weakening of the eclipsing (ring to metal donor) interaction and/or intermolecular packing forces and/or an orbital interaction favoring noneclipsing. This noneclipsing interaction might be the metal to ring "back-bonding" between the occupied metal (d_{xy}, $d_{x^2-y^2}$) orbitals and the $^3B_1$ π^* orbitals on the rings. Since the nodes of the metal d_{xy} and $d_{x^2-y^2}$ orbitals are 45° from each other, a nitrogen–center–center′–nitrogen′ torsional angle of 45° (135°) would lead to the best overlap with the $^3B_1$ π^* orbitals on the two rings. The torsional angles in **4B**, 2, and 1 are 47°, 47°, and 140°, respectively.

Intermolecular Contacts. The previous discussion has centered on electronic arguments for the configurations of 1–**4B**. Obviously we must address the issue of intermolecular contacts and especially the hydrogen bonds of 1 and **4A**. If the observed molecular configurations of 1–**4B** were due solely to intermolecular or crystal packing forces, we would expect the ring–metal–ring orientations to be random. Instead they can be readily assigned (see above) to eclipsed and noneclipsed (45°) structures.

The effects of the intermolecular hydrogen bonding in 1 and **4A** on the ring–metal–ring configuration are difficult to judge. On the one hand the contacts are 0.2 Å shorter than any other intermolecular contacts and are assumed to be attractive interactions.[16,22] On the other hand the observed bond distances and angles for the hydrogen-bonded atoms are not significantly different from the distances and angles for the other ring atoms. We can only speculate that the noneclipsed chromium compound **4B** is the electronically favored form and that the eclipsed form **4A** is observed because of the added stabilization of the hydrogen bond. The titanium complex 1 displays a torsion angle of 140°, five degrees from the proposed ideal of 135°. Again we can only speculate that this is an effect of the intermolecular hydrogen bond.

Summary

The structures of 1, 2, and 3 display the expected sandwiching of the metal between the two ligand rings. The structure of the cationic chromium complex 3 indicates that the bonding in this complex is most like the bonding in bis(benzene) metal sandwich complexes with fairly symmetric metal–ring bonding and an eclipsed orientation of the rings. For the titanium (1) and vanadium (2) complexes the structures indicate that the metal–ring bonding interactions are concentrated in the metal to ring donor interaction between the metal d_{xy} and $d_{x^2-y^2}$ orbitals and the 3B1 π^* ring orbitals. This interaction leads to asymmetric metal-ring π-coordination and a non-eclipsed ring orientation.

Acknowledgment. E.J.W. thanks Dr. F. Hollander of the Department of Chemistry X-ray Facility (CHEXRAY) for the structural determinations and Profs. R. A. Andersen and H. Vahrenkamp for helpful discussions during the preparation of this paper. This work was supported by the National Science Foundation Grant CHE-8307159.

Registry No. 1, 108534-90-3; 2, 108534-91-4; 3, 108534-94-7.

Supplementary Material Available: Tables of anisotropic thermal parameters and additional drawings (ORTEP) (7 pages); tables of F_o/F_c (35 pages). Ordering information is given on any current masthead page.

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[19] We calculate a C4–H4···N′ hydrogen bond distance of 2.55 Å from the data provided for **4A** in ref 4.

[20] a) Klabunde, K. J.; Efner, H. F. *Inorg. Chem.* **1975**, *14*, 789. b) Radonovich, L. J.; Zuerner, E. L.; Efner, H. F.; Klabunde, K. J. *Inorg. Chem.* **1976**, *15*, 2976. c) Eyring, M. W.; Zeurner, E. C.; Radonovich, L. J. *Inorg. Chem.* **1981**, *20*, 3405.

[21] Schmidt, R. E.; Massa, W. *Z. Naturforsch., B: Anorg. Chem., Org. Chem.* **1984**, *39B*, 213.

[22] As stated in the Experimental Section all hydrogen positions are uncorrected (Churchill, M. R. *Inorg. Chem.* **1973**, *12*, 1213). Corrected positions would in general lead to shorter hydrogen-bonding distances. Since we cannot say what the energy of the hydrogen bond is nor how this energy might vary with distance or contact direction, we simply report the observed value.